

Polymerization of acrylamide with diffusion-controlled termination

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Aqueous solution polymerizations of acrylamide at high monomer concentrations have been carried out using potassium persulphate as initiator in the temperature range, 20°–70°C to provide rate and molecular weight data under diffusion-controlled termination. Molecular weight development is followed by measurement of weight-average molecular weight with a low-angle, laser light-scattering photometer (Chromatix KMX6). A kinetic model which accounts for diffusion-controlled termination is developed and used to identify strategies to maximize productivity and molecular weight.

(Keywords: aqueous free-radical polymerization; acrylamide; diffusion-controlled termination; high molecular weights)

INTRODUCTION

High molecular weight polyacrylamides (PAM) are finding increasing application in areas such as flocculation and enhanced oil recovery via polymer flooding. In commercial production of PAM there is need to maximize both production rates and molecular weight and this can be done most efficiently with a comprehensive polymer reactor model.

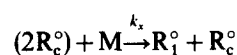
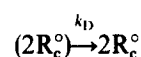
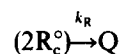
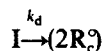
A number of authors have reported experimental studies of the aqueous solution polymerization of acrylamide using several free-radical initiator types¹. However, only a few kinetic studies included molecular weight measurements and polymerization at high monomer concentrations to high levels of conversion^{2,3}. Previous measurements did reveal the importance of diffusion-controlled termination; however, a reactor model which accounts for diffusion-controlled termination was not developed².

The objective of the present study was to develop a kinetic model for the aqueous solution polymerization of acrylamide which accounts for diffusion-controlled termination and, therefore, is applicable at high monomer concentrations and conversions. This kinetic model could then be used to develop a reactor model to investigate production strategies in the commercial temperature range, 25–70°C. Of particular interest in this regard is the production of very high molecular weight PAM at maximum productivity.

KINETIC MODELLING

The kinetics of synthesis of polyacrylamide via aqueous free-radical polymerization are adequately described by the following set of elementary reactions^{2,4}:

Initiation

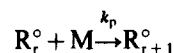


Where I, R_c° and M are initiator, initiator radical and monomer. The initiation rate (R_i) may be expressed as:

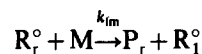
$$R_i = 2fk_d[I] \quad (1)$$

with f the initiator efficiency taking on different forms depending upon the initiator type used^{2,4}.

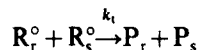
Propagation



Transfer



Termination



where R_r° is a polymer radical containing r -monomer repeat units.

A preliminary investigation revealed that long chain branching reactions via transfer to polymer and terminal double bond polymerization were negligible in the temperature range 25–79°C. It was also established that transfer to potassium persulphate was negligible in disagreement with previous work⁷. This may have been the result of following molecular weight development by laser light-scattering photometry, an absolute method and one which is more reliable than viscometry where non-

Newtonian effects have been shown to be important for high molecular weight polyacrylamides⁷.

For the case of initiation with persulphate the following rate expression has been shown to be valid^{6,7}:

$$R_p = k_{125}[I]^{1/2}[M]^{1.25} \quad (2)$$

with the lumped parameter given by:

$$k_{125} = 1.7 \times 10^{11} \exp(-16900/RT) \quad (2a)$$

with $T(K)$ and k_{125} in liter^{0.75}/(gmol^{0.75})(min). The form of equation (2) would suggest the following equation for the initiator efficiency:

$$f = 5.87 \times 10^{-3} \exp(3530/RT)[M]^{0.5} \quad (2b)$$

with the Arrhenius equation for potassium persulphate initiator given by:

$$k_d = 2.12 \times 10^{18} \exp(-33320/RT) \text{ min}^{-1} \quad (2c)$$

For the case of initiation with azobiscyanovaleric acid (ACV) the following expression for the initiator efficiency applies²:

$$f = [M]/(a + [M]) \quad (3)$$

with $a=0.97$ at 50°C and 1.20 at 40°C. The Arrhenius equation for ACV is given by:

$$k_d = 4.62 \times 10^{15} \exp(-28070/RT) \text{ min}^{-1} \quad (3a)$$

In the aqueous solution polymerization of acrylamide moderate concentrations of very high molecular weight polymer lead to chain entanglements and diffusion-controlled termination. This further leads to an acceleration in polymerization rate and moderate increases in molecular weights for isothermal polymerizations (molecular weight development is largely controlled by transfer to monomer). The dependence of the diffusion-controlled termination constant on polymer concentration and temperature can be adequately expressed by the empirical equation⁵⁻⁸:

$$(k_{tc}/k_t)^{1/2} = \exp(AW_p + BW_p^2 + CW_p^3) \quad (4)$$

with

$$A = a_1 + a_2 T \quad (4a)$$

$$B = b_1 + b_2 T \quad (4b)$$

and

$$C = c_1 + c_2 T \quad (4c)$$

The adjustable parameters $a_1, a_2, b_1, b_2, c_1, c_2$ are found by fitting isothermal conversion/time curves. This empirical form gives coefficients which depend linearly upon temperature permitting more reliable interpolation and extrapolation. W_p is the weight fraction of polymer.

Instantaneous molecular weight distribution and chain length averages are given by:

$$w(r) = \tau^2 r \exp(-\tau r) \quad (5)$$

$$r_N = 1/\tau \quad (5a)$$

$$r_w = 2/\tau \quad (5b)$$

$$r_z = 3/\tau \quad (5c)$$

$$r_{z+1} = 4/\tau \quad (5d)$$

where

$$\tau = k_t R_p / k_p^2 [M]^2 + k_{tm} / k_p$$

The accumulated molecular weight distribution ($\bar{w}(r)$) and chain length averages are given by:

$$\bar{w}(r) = \frac{1}{x} \int_0^x w(r) dx \quad (6)$$

$$\bar{r}_N = x \int_0^x (1/r_N) dx = x \int_0^x \tau dx \quad (6a)$$

$$\bar{r}_w = \int_0^x r_w dx / x = 2 \int_0^x (1/\tau) dx / x \quad (6b)$$

$$\bar{r}_z = (6/\bar{r}_w) \int_0^x (1/\tau^2) dx / x \quad (6c)$$

$$\bar{r}_{z+1} = (24/\bar{r}_w \bar{r}_z) \int_0^x (1/\tau^3) dx / x \quad (6d)$$

EXPERIMENTAL

Acrylamide purchased from Eastman Kodak Co. (Rochester, N.Y.) was twice recrystallized from chloroform and stored in dark bottles in a refrigerator before polymerization. The initiator, potassium persulphate was recrystallized twice from doubly-distilled water. The water used as solvent for the polymerization was doubly distilled with the final distillation carried out with alkaline potassium permanganate. Both freeze/thaw techniques⁵ and N₂ bubbling techniques^{2,7} were used to remove oxygen from the acrylamide/water solution before polymerization. It was observed that less than 1% conversion

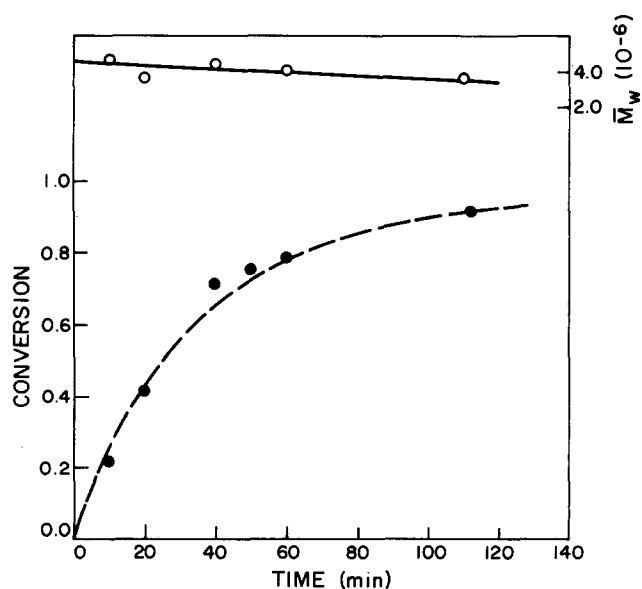


Figure 1 Polymerization of acrylamide—rate and molecular weight development ($T=70^\circ\text{C}$; $[M]_0=0.75 \text{ ml l}^{-1}$; $[I]_0=1.2 \times 10^{-4} \text{ m l}^{-1}$; —, O₂ removal by N₂ bubbling' (---, predicted with chemically-controlled termination)

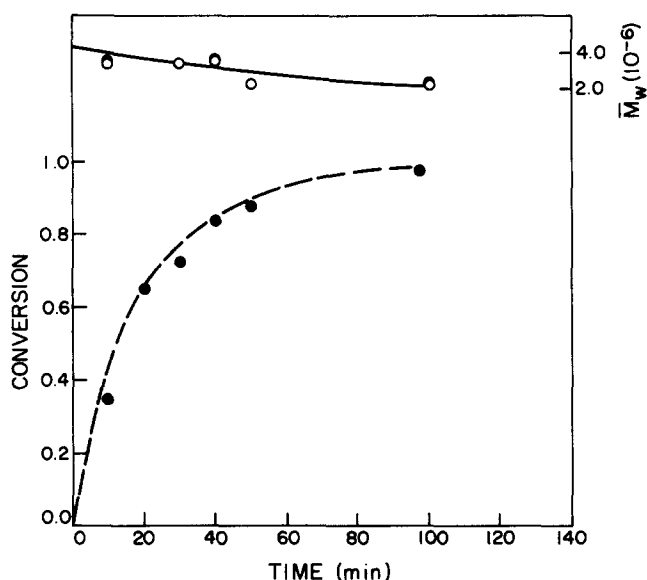


Figure 2 Polymerization of acrylamide-rate and molecular weight development ($T=70^{\circ}\text{C}$; $[M]_0=0.75\text{ m l}^{-1}$; $[I]_0=5.2\cdot 10^{-4}\text{ m l}^{-1}$; O_2 removed by N_2 bubbling) (---, predicted with chemically-controlled termination)

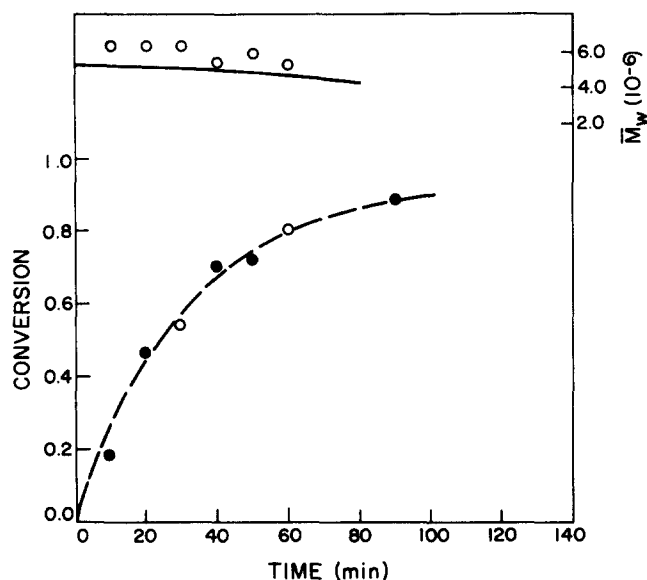


Figure 3 Polymerization of acrylamide-rate and molecular weight development ($T=70^{\circ}\text{C}$; $[M]_0=1.0\text{ m l}^{-1}$; $[I]_0=1.3\cdot 10^{-4}\text{ m l}^{-1}$; O_2 removed by N_2 bubbling) (---, predicted with chemically-controlled termination)

occurred during the freeze/thaw process to remove O_2 . Pyrex ampoule reactors (12 mm o.d., 10 mm i.d. and 170–300 mm long) gave isothermal polymerizations². The reactions were initiated by placing the sealed ampoules containing water, monomer and initiator into a constant temperature bath. The reaction was quenched by placing the hot ampoule into liquid nitrogen. Conversion of monomer was measured by size exclusion chromatography². To recover polymer for measurement of \bar{M}_w by light scattering, the broken ampoule was transferred into approximately ten times its volume of distilled water containing hydroquinone, an inhibitor. The diluted solution was added dropwise to methanol with vigorous stirring (using a magnetic stirrer). The precipitated polymer was filtered, washed with acetone and dried to constant weight at 50°C under vacuum. The weight-

average molecular weight of the polymer was measured by low-angle, laser light-scattering photometry using the Chromatix KMX6 at a wavelength of 632.8 nm. A recommended specific refractive index increment for polyacrylamide in water ($dn/dc=0.1829$) was used in the calculation of \bar{M}_w ¹.

The experimental conditions used for all of the polymerizations are given in the captions of Figures 1–9.

RESULTS AND DISCUSSION

The experimental conversion/time curves and molecular weight data (\bar{M}_w) and model predictions are summarized in Figures 1–9. The dotted conversion/time curves are model curves where the termination reaction is chemically controlled (depends on reaction temperature alone). The

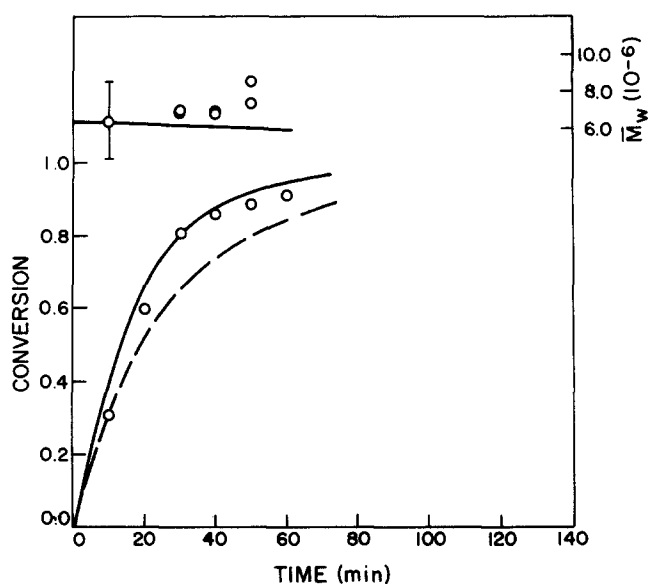


Figure 4 Polymerization of acrylamide-rate and molecular weight development ($T=70^{\circ}\text{C}$; $[M]_0=2.2\text{ m l}^{-1}$; $[I]_0=1.3\cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

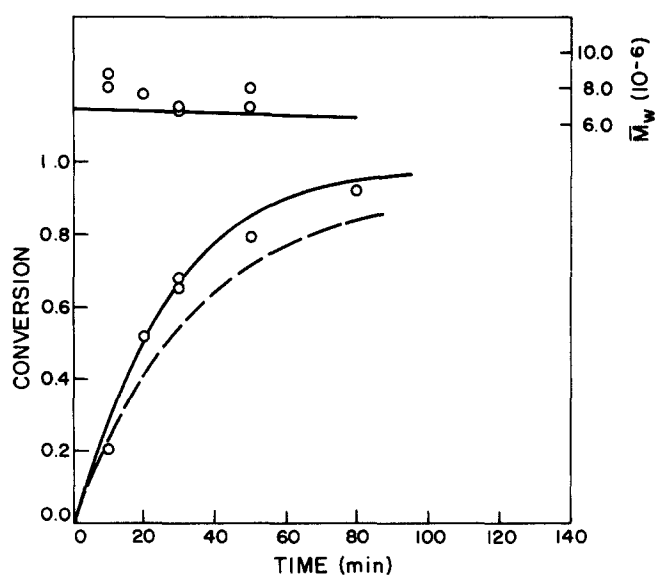


Figure 5 Polymerization of acrylamide-rate and molecular weight development ($T=70^{\circ}\text{C}$; $[M]_0=2.2\text{ m l}^{-1}$; $[I]_0=0.65\cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

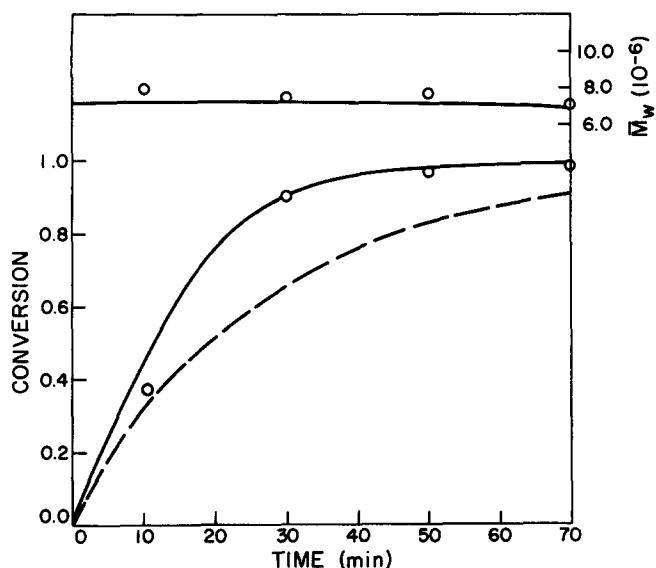


Figure 6 Polymerization of acrylamide-rate and molecular weight development ($T=60^{\circ}\text{C}$; $[M]_0=3.4\text{ m l}^{-1}$; $[I]_0=5.2 \cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

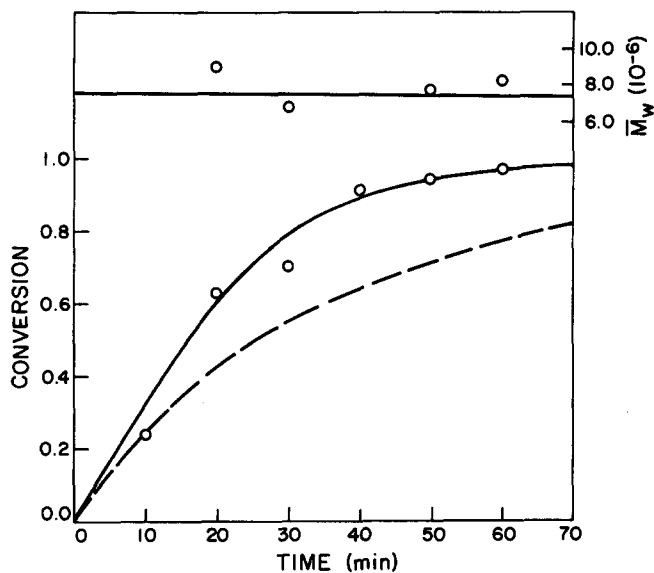


Figure 7 Polymerization of acrylamide-rate and molecular weight development ($T=60^{\circ}\text{C}$; $[M]_0=3.4\text{ m l}^{-1}$; $[I]_0=2.6 \cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

solid conversion/time curves are for the model when diffusion-controlled termination is accounted for. In Figures 1-3, the solid conversion/time curves are not shown as the agreement with the dotted curves is almost perfect. The magnitude of the difference between solid and dotted conversion/time curves can be taken as a qualitative measure of the importance of diffusion-controlled termination. The error bars on molecular weight and conversion measurements show extreme values and an average value.

Equation (7) shows the parameters established for the kinetic model and the temperature dependence of A, B, C.

$$A = 11.22 - 1.67 \cdot 10^{-2} T \quad (7a)$$

$$B = 12.82 - 2.22 \cdot 10^{-2} T \quad (7b)$$

$$C = 12.49 - 2.33 \cdot 10^{-2} T \quad (7c)$$

Equations (8) and (9) are Arrhenius equations for the other kinetic model parameters.

$$k_p/k_t^{1/2} = 139.0 \exp(-2002/RT) \quad (8)$$

$$k_{tm}/k_p = 1.73 \times 10^{-4} \exp(-1609/RT) \quad (9)$$

Equations (8) and (9) are shown plotted in Figure 10 with experimental data measured herein and elsewhere^{2,4}. The bubbling and freeze-thaw techniques for oxygen removal are comparable and within experimental error give the same conversion/time data.

Finally, the kinetic model was used to predict the effect of polymerization temperature and time on \bar{M}_w for an isothermal batch polymerization taken to a conversion of 98%. These predictions are shown in Figure 11 along with

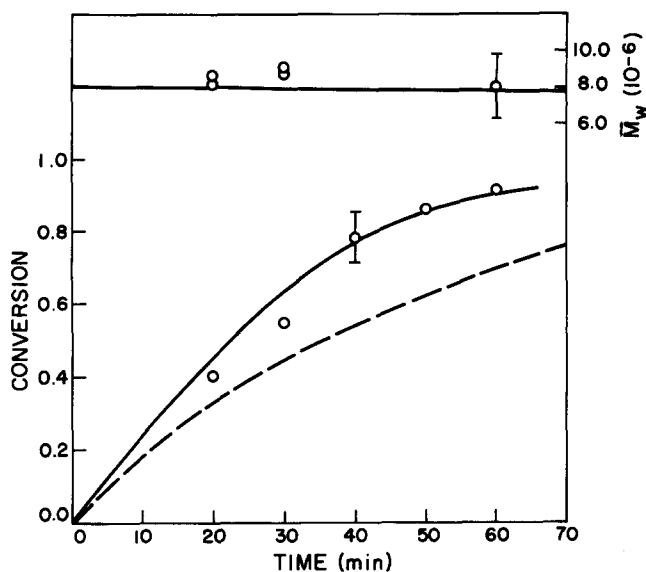


Figure 8 Polymerization of acrylamide-rate and molecular weight development ($T=60^{\circ}\text{C}$; $[M]_0=3.4\text{ m l}^{-1}$; $[I]_0=1.3 \cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

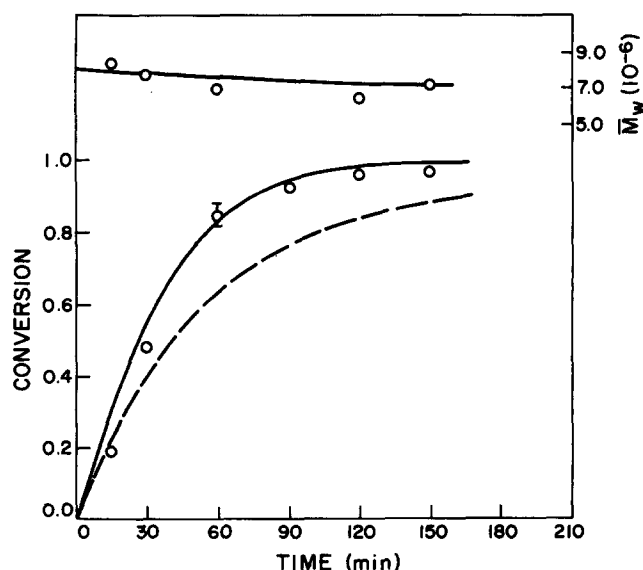


Figure 9 Polymerization of acrylamide-rate and molecular weight development ($T=40^{\circ}\text{C}$; $[M]_0=2.5\text{ m l}^{-1}$; $[I]_0=33.0 \cdot 10^{-4}\text{ m l}^{-1}$) (---, predicted with chemically-controlled termination, —, predicted with diffusion-controlled termination)

ultimate \bar{M}_w values (dotted horizontal lines) which are possible when transfer to monomer dominates molecular weight development. This condition occurs at low radical initiation and termination rates. It is clear that the effect of radical initiation and termination on molecular weight development is much less pronounced at lower temperatures. This is largely the effect of diffusion-controlled termination which is more pronounced with higher molecular weight chains at lower temperatures.

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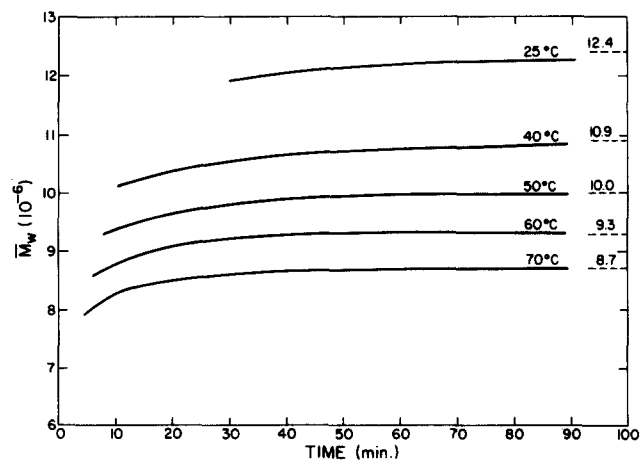


Figure 11 Kinetic model predictions for isothermal batch polymerization of acrylamide. Effect of temperature and polymerization time on weight-average molecular weight for a terminal conversion of 98% (50% solids)

experimental programme of this study is gratefully acknowledged.

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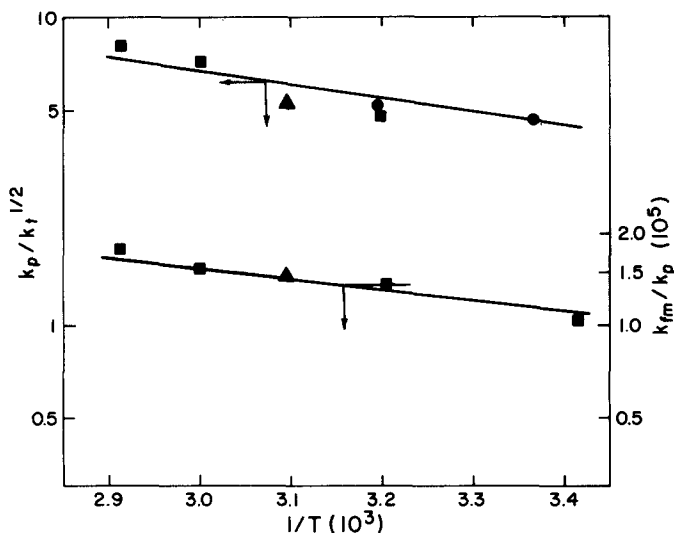


Figure 10 Kinetic model parameters (■, present study; ●, Dainton and Tordoff; ▲, Ishige and Hamielec) (—, equations 8 and 9)